HYDROGEN ION STUDIES
IN
SOME PHOSPHATE SOLUTIONS.

By

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Submitted to the Department of Chemistry and the Faculty of the Graduate School of the University of Kansas in Partial fulfillment of the requirements for the degree of

MASTER OF ARTS.

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December, 1923.

I wish to express my thanks to Dr. H. P. Cady for his direction of this work and for his many helpful suggestions and to Dr. H. M. Elsey for his co-operation and for his assistance in designing and making the apparatus used.

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INTRODUCTION.

Although many of the buffer solutions in use at the present time are phosphate mixtures and depend on the fact that salts of weak acids, such as phosphoric acid, in the presence of some of the corresponding acid, resist changes in their hydrogen ion concentration when small quantities of acids or alkalies are added, yet little data seems to be at hand as to the hydrogen ion concentrations of various dilutions of the phosphate salts themselves and of their mixtures with phosphoric acid.

Ringer[1] titrated phosphoric acid against sodium hydroxide. On plotting the hydrogen ion concentrations against quantity of alkali added, he obtained a curve having sharp breaks corresponding to NaH_2PO_4 and Na_2HPO_4, but none for Na_3PO_4. This latter phenomenon he attributes to almost complete hydrolysis of the tri-sodium salt. Reference to his work will be made again later.

Henderson[2] worked chiefly on mixed solutions of the mono- and di-sodium phosphates. He evolved a complicated theory as to ionization and hydrolysis in these solutions, and also titrated di-sodium phosphate against phosphoric acid at various temperatures, using both methyl orange and phenolphthalein as indicators.

Prideaux[3] says that the second and third dissociation constants of phosphoric acid govern the hydrogen ion con-

centrations of solutions of the phosphates. He, likewise, titrated sodium hydroxide against phosphoric acid, using varying amounts of the base to a fixed volume of acid and diluting to a fixed volume after each addition.

The phosphates were chosen as the subject of this investigation chiefly because they afford a means of studying the effect of the substitution of metal atoms for three successive hydrogen atoms. Moreover, the weakness of phosphoric acid furnishes an opportunity to observe the relation of hydrolysis to the hydrogen ion concentration of salts.

PREPARATION OF THE PHOSPHATES.

The phosphoric acid solution was made approximately 0.4 molar by using 56 c.c. of the 85% H_3PO_4 (syrupy phosphoric acid) and making the solution up to two liters. The following results were obtained upon analysis, precipitating the phosphate as $MgNH_4PO_4$, and igniting to $Mg_2P_2O_7$ in a Gooch crucible in an electric furnace. Duplicate 5 c.c. samples were used.

	Weight of $Mg_2P_2O_7$	Gm. H_3PO_4 per c.c. of Sol.	Gram Moles H_3PO_4 per Liter.	Normality
I	0.2046	0.036034	0.36475	1.10235
II	0.2041	0.035946	0.36656	1.109968
Mean		0.035990	0.367005	1.101015

The monosodium hydrogen phosphate was made by dissolving a gram mole (358 grams) of the stock $Na_2HPO_4.12H_2O$ in the minimum amount of boiling water[5] and adding a gram mole (68 c.c.) of the 85% H_3PO_4, specific gravity 1.709 at 17° C. The mixture was boiled in a weighed beaker until its weight corresponded to two gram moles of $NaH_2PO_4.2H_2O$. Before this weight was reached, the hydrogen ion concentration of the mixture had fallen so low that even the liquid solution failed to redden dry blue litmus paper.

According to Imadsu[6], $NaH_2PO_4.2H_2O$ is stable up to 40.8° C, when it changes to the monohydrate which loses its mole of water at 57.4° C. The salt remained dissolved in the two moles of water of crystallization while hot, but separated out on cooling.

Although a good crop of crystals was obtained, the mother liquor was such a heavy syrup that it was impossible to effect a separation. The crystals remained gummy even after repeated washings with absolute alcohol, and finally had to be dried for several days in an oven at 60° C. A sample of the salt weighing 16.106 grams was made up to a liter with carbon-dioxide-free water, prepared by drawing through it a stream of air from successive towers of pumice stone coated with sulfuric acid, soda lime, and cotton wool. An analysis, made as described for the phosphoric acid, showed that the salt was probably completely dehydrated at 60° C, the temperature used for drying it.

	Weight of Sample (25 cc.)	Weight of $Mg_2P_2O_7$	Gram of NaH_2PO_4 per gram Solution	Gram of NaH_2PO_4 per c.c. Solution	Gram Moles NaH_2PO_4 per Liter.
I	25.218	0.3608	0.015428	0.015563	0.12963
II	25.173	0.3592	0.015465	0.015572	0.12971
Mean			0.0154465	0.0155675	0.12967

The disodium hydrogen phosphate used was purified from the stock $Na_2HPO_4.12H_2O$ by recrystallizing it three times from boiling water, and drying the crystals first between filter papers and then on a tile in a container kept closed to prevent dessication. One-tenth of a mole of the salt, 35.831 grams, was weighed out and made up to a liter with carbon-dioxide-free water. The following results were obtained by the same method of analysis as before.

	Weight of Sample (25 cc.)	Weight of $Mg_2P_2O_7$	Gram of Na_2HPO_4 per gram Solution	Gram of Na_2HPO_4 per c.c. Solution	Gram Moles Na_2HPO_4 per Liter.
I	24.9570	0.2825	0.01444	0.014416	0.10149
II	25.3034	0.2822	0.01423	0.014402	0.10139
Mean			0.014335	0.014409	0.10144

The trisodium phosphate crystals, made by heating disodium hydrogen phosphate with excess sodium hydroxide in concentrated solution for ten hours at 77° C[7], were washed

with 95% alcohol, which seemed to produce dessication. This was manifested by a change in the appearance of the crystals from transparency to opacity. The salt was kept under 95% alcohol until required for use, when it was dried in the oven at 100° C. Considering the salt as anhydrous, since the dessication produced by the alcohol was thought to be complete, a tenth-mole, 16.403 grams of the salt was made up to a liter with carbon dioxide-free water. These results were obtained by gravimetric analysis as previously described.

	Weight of Sample (25 cc.)	Weight of $Mg_2P_2O_7$	Gram of Na_3PO_4 per gram Solution	Gram of Na_3PO_4 per c.c. Solution	Conc. in Gram Mole per Liter.
I	25.315	0.2525	0.014692	0.014878	0.090698
II	25.265	0.2512	0.014645	0.014806	0.090258
Mean			0.0146685	0.014842	0.090478

If the salt weighed out had been anhydrous Na_3PO_4, the analysis should have showed about 0.0164 gram of the salt per c.c. of solution instead of 0.014842 gram as found. If the salt as used was the monohydrate, the 1.8016 gram of water present in the one-tenth mole of the salt would practically account for the discrepancy.

STANDARD ACID AND ALKALI.

The sodium hydroxide used was made up first in very concentrated solution and left to allow any sodium carbon-

ate to deposit out. The solution did not become clear even after several days' standing, and it also proved impossible to freeze out pure NaOH. The thick solution was finally filtered by suction through alundum filter crucibles, made up to approximately half-normal solution and standardized against hydrochloric acid solution, using methyl orange as indicator.

c.c. HCl	c.c. NaOH	Ratio HCl to NaOH
45.54	19.93	2.2849
45.14	19.76	2.2844
45.37	19.87	2.2834
		2.2842 Mean

The hydrochloric acid was 0.21164 normal, making the sodium hydroxide 2.2842 x 0.21164 or 0.48353 times normal.

The HCl was standardized gravimetrically by precipitation as AgCl.

c.c. HCl	Weight of AgCl	Gram HCl/c.c.
10	0.3024	0.0077471
10	0.3032	0.0077700
40	1.2112	0.0077538
40	1.2092	0.0076911
40	1.2124	0.0077065
40	1.2097	0.0076943
25	0.7563	0.0076961
25	0.7583	0.0077164
	Mean	0.0077183

The solution contained 0.0077183 gram of HCl per c.c., making it 0.0077183 ÷ 0.03647 = 0.21164 times normal.

ELECTRODES AND ELECTRODE VESSELS.

The calomel half-cell was of the saturated potassium chloride type. The potassium chloride was purified by dissolving it in water, filtering, boiling until crystals just began to appear in the hot solution, and then passing in hydrogen chloride gas made by dropping concentrated sulfuric acid slowly into concentrated hydrochloric acid at room temperature. The product was washed once with a small amount of cold water, and then heated until its solution no longer reddened blue litmus. The mercury was distilled in a slow current of air to oxidize impurities. The calomel was shaken repeatedly with large volumes of water to dissolve out any mercuric chloride present.

Electrolytic hydrogen gas was used. It was passed over the hot filaments of an electric light bulb having two side arms, to burn out any traces of oxygen present. The rubber tubing through which the hydrogen passed had been previously boiled in strong sodium hydroxide solution to remove sulfur compounds which might seriously poison the hydrogen electrode.

For the hydrogen electrode itself, a narrow strip of thin platinum foil was sealed into a piece of glass tubing. Contact was made by mercury. The polished platinum was coated with platinum black by making it the cathode in a

three per cent solution of platinic chloride containing one-fortieth of one per cent of lead chloride and using a platinum wire as anode. After coating, the electrode was electrolyzed for a few minutes as cathode in a dilute sulfuric acid solution to remove chlorides.

In Figure I are shown the hydrogen electrode vessel and the calomel half-cell, both of which were made especially for this work by Dr. H. M. Elsey. The hydrogen gas enters the gas jacket, B, of the electrode vessel at, A, and escapes into a beaker of water at, C. The cork, H, carries the glass tube with its platinum foil electrode, which is half immersed in the solution and half in contact with the hydrogen. In the calomel electrode, D, connects with the reservoir of saturated potassium chloride placed above it. By means of the stopcock, E, the capillary tube, T, can be flushed with fresh potassium chloride solution, and filled with it just to the lower end of the capillary, G, before every determination. The two electrode vessels are connected by rubber tubing at, H.

POTENTIOMETER.

For the determination of the potential difference set up by the platinized platinum-hydrogen electrode dipping into the phosphate solution against the saturated potassium chloride-calomel electrode, use was made of the potentiometer method, balancing the potential difference under measurement against an opposing, known, potential difference.

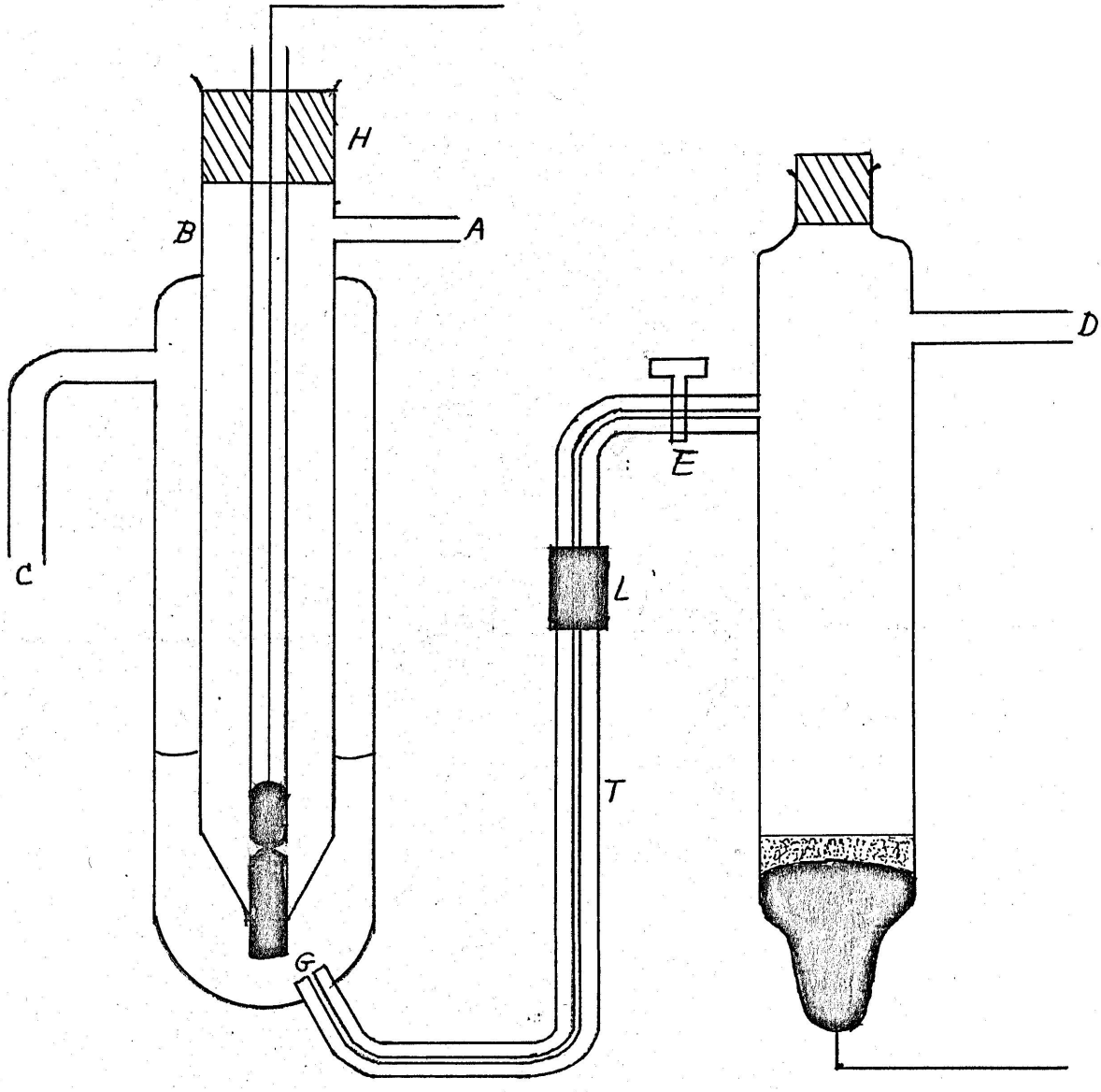

FIGURE I

The apparatus used consisted of a Leeds and Northrup potentiometer wired as shown in Figure II. B, the source of electromotive force, is an ordinary dry cell. The standard cell, SC, is a Marion Eppley unsaturated cadmium cell, whose potential is 1.0188 volts and which has a practically negligible temperature coefficient. S is a double throw switch. K is the key by which current can be made to flow momentarily through the galvanometer G. M and M' are resistance boxes whose scales are graduated to read in volts instead of ohms. For this purpose, the fall of potential across each coil of M is made one-tenth of a volt, and the resistance wire in M' is graduated in small known fractions of a volt, making it possible to read the potential difference accurately to the tenth of a millivolt. R is a protective resistance box used to aid in balancing the standard cell arm of the circuit. E is the cell formed by the calomel half-cell and the hydrogen electrode dipping into the phosphate solution.

CALCULATIONS.

Results were originally calculated in terms of pH value, the logarithm on the base ten of the reciprocal of the hydrogen ion concentration, cH, expressed in gram equivalents per liter.

$$pH = \log \frac{1}{cH} = \frac{E - F}{d}$$

E is the measured electromotive force. F^8 is the potential difference between the saturated calomel electrode

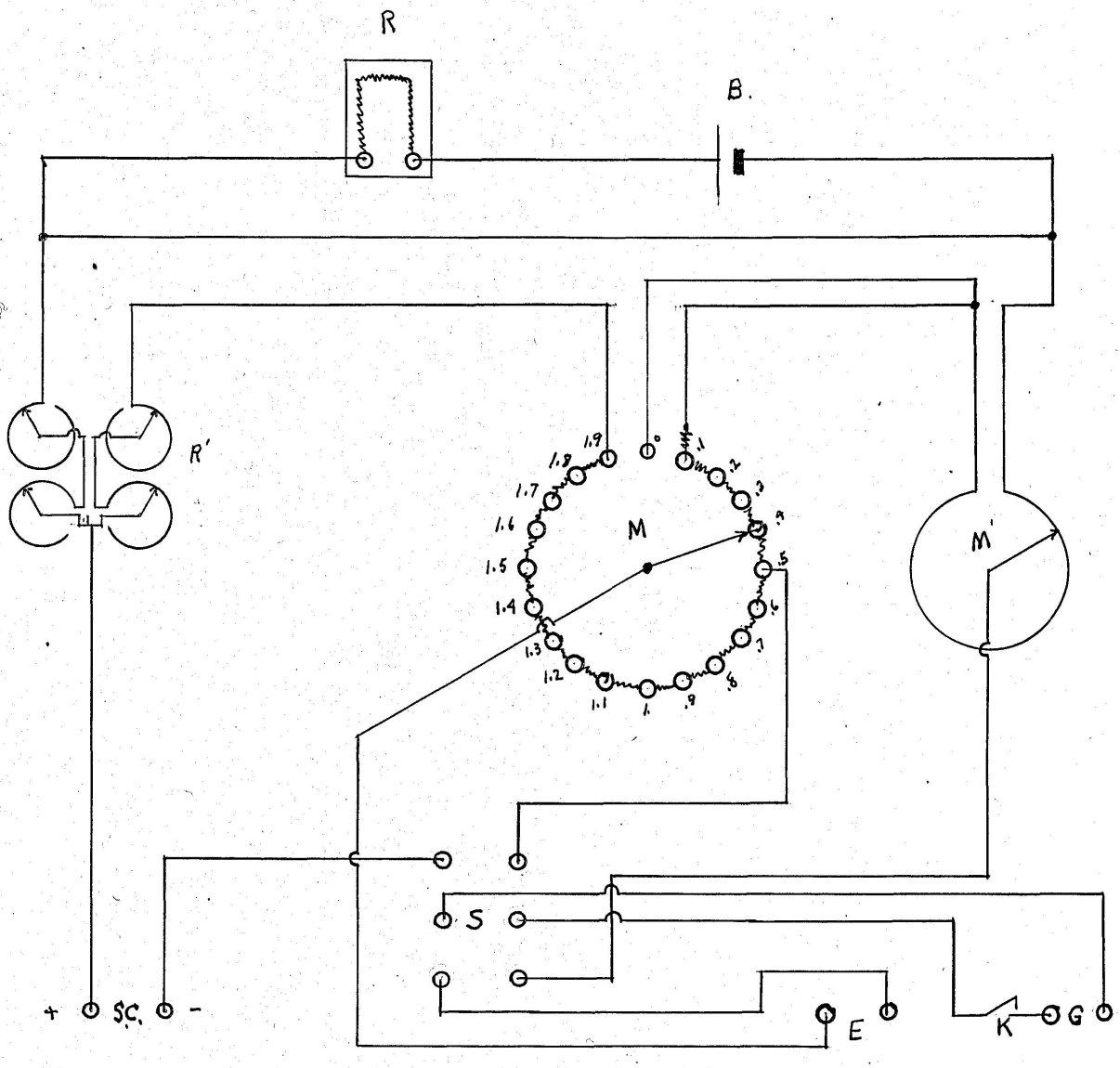

FIGURE II

and that which would be given by a solution normal with respect to hydrogen ions and a hydrogen electrode under one atmospheric pressure of hydrogen, this latter potential difference being defined as zero. The quantity, d^8, is also a function of the temperature and involves the gas constant, R, the Faraday constant, and factors for changing from volts to millivolts and from natural logarithms to logarithms on the base ten.

$$d = \frac{RT \times 1000}{nF \times 0.4343}$$

Since all of these calculations are based on the assumption that the hydrogen gas is under a pressure of 76 centimeters, corrections must be made for deviations from this value. The barometric pressure must be corrected for temperature[9] to obtain the reading in terms of mercury at zero degrees centigrade, and for the vapor pressure of water at the temperature of the reading. This value for the vapor pressure is sufficiently close an approach to the actual value for the solution which would, of course, be a little lower than the corresponding value for pure water. In the cell,

$$Hg \mid HgCl \mid KCl \mid H^+ \mid Pt \mid H_2,$$

if the hydrogen is under diminished pressure, the E.M.F. of the cell is too low. Hence the correction must be applied to make the E.M.F. larger than observed, and the equations take the following forms:

$$\frac{E + Ebar - F}{d} = pH$$

$$Ebar = \frac{RT \times 1000}{2nF} \log \frac{760}{X}$$

Ebar is the barometric voltage correction in millivolts, X is the corrected barometer reading in millimeters, and R, T, n and F have their usual significances.

pH values and cH values were interchanged by these formulae:

Let $pH = x.y$

Then $cH = \text{antilog } (1 - y) \times 10^{-(x + 1)}$

Conversely, if $cH = a \times 10^{-b}$

$pH = (b - 1) + (1 - \log a)$

The curves on Plate I show the pH values of various concentrations of the three sodium phosphates plotted as ordinates against the logarithms of the concentrations as abscissae. For these determinations, the original solutions of the salts were diluted two fold, tenfold, etc. It will be noted that, as might be expected, the hydrogen ion concentrations for corresponding dilutions decrease quite markedly with the replacement of hydrogen by sodium. The NaH_2PO_4 solutions are in the acid range, the Na_2HPO_4 in the alkaline range, and the Na_3PO_4 solutions are decidedly basic. It may also be seen that, with increasing dilution, the pH values for all three solutions tend to approach that of water, which is represented by the heavy black horizontal line. This indicates that the dissociation does not increase rapidly enough with

increasing dilution to compensate the smaller amount of salt per unit volume. The following table gives the data obtained in these determinations.

Plates II, III and IV show the effect of adding phosphoric acid to solutions of the mono-, di- and tri-sodium phosphates respectively. In every case, the concentrations of phosphoric acid added to each of the three dilutions of each salt are 0, 0.001, 0.01, 0.05 and 0.1 gram mole per liter. The cube roots of these concentrations are plotted as abscissae against the pH values of the mixtures as ordinates. For the di- and tri-sodium phosphates, the salt concentrations represented are 0.05, 0.01 and 0.001 molar, and for the monosodium hydrogen phosphate, 0.033, 0.01 and 0.001 molar.

The pH value for the mixture of salt and acid lies, of course, in every case, between that of the pure acid at that particular concentration and that of the salt under the same conditions. However, some interesting discrepancies are noted in comparing the results. One might expect these reactions to take place on the addition of the acid to the salts.

$$Na_2HPO_4 + H_3PO_4 = 2NaH_2PO_4$$

$$Na_3PO_4 + 2H_3PO_4 = 3NaH_2PO_4$$

$$2Na_3PO_4 + H_3PO_4 = 3Na_2HPO_4$$

This would indicate that a solution 0.01 molar with respect to both the disodium salt and the acid should have the same pH value as a solution 0.02 molar with respect to the mono-

NaH_2PO_4

Conc. in Gm. Moles per Liter	Log. Conc.	Temp. °C	Press. Cm.	E.M.F. Milli-volts.	pH	cH
0.12967	9.11 - 10	28.5	73.29	603.15	6.038	9.163×10^{-7}
0.064835	8.81 - 10	29.0	73.29	610.35	6.157	6.966×10^{-7}
0.025934	8.41 - 10	29.0	73.29	618.20	6.288	5.153×10^{-7}
0.012967	8.11 - 10	28.7	73.54	622.30	6.359	4.376×10^{-7}
0.004322	7.63 - 10	29.3	73.54	628.40	6.454	3.516×10^{-7}
0.0025934	7.41 - 10	29.7	73.54	634.10	6.547	2.838×10^{-7}
0.001854	7.27 - 10	30.5	73.54	640.10	6.643	2.275×10^{-7}
0.0012967	7.11 - 10	31.0	73.54	644.90	6.717	1.919×10^{-7}

Na_2HPO_4

Conc. in Gm. Moles per Liter.	Log. Conc.	Temp. °C	Press. Cm.	E.M.F. Milli-volts.	pH	cH
0.10144	9.01 - 10	31.2	73.54	777.50	8.902	1.253×10^{-9}
0.05072	8.71 - 10	31.5	73.54	770.55	8.781	1.656×10^{-9}
0.020288	8.31 - 10	30.00	73.38	760.85	8.656	2.208×10^{-9}
0.010144	8.01 - 10	30.0	73.35	754.35	8.549	2.825×10^{-9}
0.003381	7.53 - 10	29.0	73.15	731.40	8.179	6.622×10^{-9}
0.0020288	7.31 - 10	30.0	73.21	724.25	8.049	8.933×10^{-9}
0.001449	7.16 - 10	29.8	73.48	711.60	7.838	1.452×10^{-8}
0.0010144	7.01 - 10	30.0	73.48	699.75	7.640	2.291×10^{-8}

Na_3PO_4

Conc. in gm. Moles per Liter.	Log. Conc.	Temp. °C	Press. Cm.	E.M.F. Milli-volts.	pH	cH
0.090478	8.96 - 10	26.0	73.38	960.30	12.083	8.261×10^{-13}
0.045239	8.66 - 10	27.5	73.38	951.55	11.891	1.285×10^{-12}
0.018096	8.26 - 10	27.8	73.37	942.55	11.734	1.845×10^{-12}
0.0090478	7.96 - 10	28.2	73.32	929.90	11.513	3.069×10^{-12}
0.0030159	7.48 - 10	28.5	73.32	901.00	11.022	9.506×10^{-12}
0.0018096	7.26 - 10	30.0	73.08	875.85	10.573	2.673×10^{-11}
0.0012925	7.11 - 10	30.5	73.08	861.70	10.327	4.710×10^{-11}
0.00090478	6.96 - 10	28.5	73.29	853.30	10.226	5.943×10^{-11}

sodium salt alone. The following table gives a table of the results obtained, chiefly from the curves.

Solution of Salt + Acid	pH	Solution of Salt Alone	pH
$0.05Na_2HPO_4 + 0.01H_3PO_4$	3.904	$0.1NaH_2PO_4$	6.05
$0.01Na_2HPO_4 + 0.01H_3PO_4$	4.417	$0.02NaH_2PO_4$	6.25
$0.001Na_2HPO_4 + 0.001H_3PO_4$	4.656	$0.002NaH_2PO_4$	6.56
$0.05Na_3PO_4 + 0.025H_3PO_4$	8.62	$0.075Na_2HPO_4$	8.86
$0.01Na_3PO_4 + 0.005H_3PO_4$	7.50	$0.015Na_2HPO_4$	8.65
$0.01Na_3PO_4 + 0.02H_3PO_4$	3.70	$0.03NaH_2PO_4$	6.29
$0.001Na_3PO_4 + 0.002H_3PO_4$	6.30	$0.003NaH_2PO_4$	6.51

It was suspected that the differences might be due to the time factor involved in these reactions. However, the pH value of a solution containing equimolecular proportions of disodium hydrogen phosphate and phosphoric acid failed to change with the passage of time, even after a lapse of five weeks. The phosphoric acid solution used failed to give tests for sulfate, nitrate, metaphosphate and phosphite ions. A very slight precipitate was produced with silver nitrate in acid solution, but a quantitative chloride determination failed to give a weighable quantity.

On the following page are listed the mixtures which have pH values approximating seven, the value for pure water:

Solution	pH
0.05 molar Na_2HPO_4 + 0.01 molar H_3PO_4	7.145
0.01 molar Na_2HPO_4 + 0.001 molar H_3PO_4	7.371
0.05 molar Na_3PO_4 + 0.05 molar H_3PO_4	7.002
0.01 molar Na_3PO_4 + 0.01 molar H_3PO_4	7.162
0.001 molar Na_3PO_4 + 0.001 molar H_3PO_4	7.337

In the case of the tri-sodium phosphate, which is commonly considered to be practically completely hydrolyzed, the effect seems to be that of mixing equivalent amounts of acid and base with the formation of a compound which is not hydrolyzed.

The following tables give the data obtained in the investigations on these mixtures of the three salts with phosphoric acid. The values for the salts alone are taken from the curves on Plate I.

Gm. Moles H_3PO_4 per Liter.	Temp. °C	Press. Cm.	E.M.F. Milli-volts.	pH	cH
		0.033 molar NaH_2PO_4 + H_3PO_4			
0.00	31.5	73.48	616.75	6.245	5.689×10^{-7}
0.001	28.5	73.48	607.45	6.112	7.727×10^{-7}
0.01	33.0	73.48	434.40	3.227	5.929×10^{-4}
0.05	27.5	73.48	369.75	2.131	7.396×10^{-3}
0.1	33.0	73.50	352.50	1.874	1.337×10^{-2}
		0.1 molar NaH_2PO_4 + H_3PO_4			
0.00	(0.1 molar NaH_2PO_4 alone)			6.360	4.365×10^{-7}
0.001	31.5	73.48	597.57	5.928	1.180×10^{-6}
0.01	32.0	73.48	395.20	2.578	2.642×10^{-3}
0.05	30.6	73.48	359.05	1.972	1.054×10^{-2}
0.1	29.0	73.48	341.95	1.676	2.109×10^{-2}
		0.001 molar NaH_2PO_4 + H_3PO_4			
0.00	(0.001 molar NaH_2PO_4 alone)			6.800	1.585×10^{-7}
0.001	31.0	73.67	438.15	3.286	5.176×10^{-4}
0.01	31.5	73.50	389.25	2.477	3.334×10^{-3}
0.05	31.5	73.50	350.25	1.831	1.476×10^{-2}
0.1	30.5	73.67	337.40	1.611	2.449×10^{-2}

Gm. Moles H_3PO_4 per Liter	Temp. °C	Press. Cm.	E.M.F. Millivolts.	pH	cH
		0.05 molar Na_2HPO_4 + H_3PO_4			
0.00	(0.05 molar Na_2HPO_4 alone)			8.781	1.656×10^{-7}
0.001	30.0	73.32	721.90	8.009	9.795×10^{-9}
0.01	30.0	73.32	670.00	7.145	7.162×10^{-8}
0.05	29.0	73.32	475.40	3.904	1.248×10^{-4}
0.1	28.3	73.32	383.35	2.364	4.326×10^{-3}
		0.01 molar Na_2HPO_4 + H_3PO_4			
0.00	(0.01 molar Na_2HPO_4 alone)			8.549	2.825×10^{-9}
0.001	25.7	73.70	680.80	7.371	4.256×10^{-8}
0.01	25.5	73.70	505.90	4.417	3.829×10^{-5}
0.05	25.2	73.70	368.30	2.089	8.147×10^{-3}
0.1	24.8	73.70	346.80	1.723	2.382×10^{-2}
		0.001 molar Na_2HPO_4 + H_3PO_4			
0.00	(0.001 molar Na_2HPO_4 alone)			7.640	2.291×10^{-8}
0.001	26.0	73.70	519.60	4.651	2.234×10^{-5}
0.01	25.5	73.70	382.30	2.329	4.689×10^{-3}
0.05	25.8	73.70	350.30	1.793	1.611×10^{-2}
0.1	25.8	73.70	337.00	1.569	2.698×10^{-2}

Gm. Moles H_3PO_4 per Liter	Temp. °C	Press. Cm.	E.M.F. Milli-volts.	pH	cH
			0.05 molar Na_3PO_4 + H_3PO_4		
0.00	(0.05 molar Na_3PO_4 alone)			12.120	7.586×10^{-13}
0.001	31.5	73.70	953.90	11.871	1.346×10^{-12}
0.01	30.0	73.70	928.80	11.452	3.352×10^{-12}
0.05	29.6	73.70	661.30	7.002	9.954×10^{-8}
0.1	28.5	73.70	585.70	5.748	1.787×10^{-6}
			0.01 molar Na_3PO_4 + H_3PO_4		
0.00	(0.01 molar Na_3PO_4 alone)			11.550	2.818×10^{-12}
0.001	31.0	73.50	887.50	10.742	1.811×10^{-11}
0.01	31.0	73.50	671.70	7.162	6.887×10^{-8}
0.05	31.8	73.50	378.75	2.293	5.093×10^{-3}
0.1	31.5	73.50	355.30	1.915	1.216×10^{-2}
			0.001 molar Na_3PO_4 + H_3PO_4		
0.00	(0.001 molar Na_3PO_4 alone)			10.220	6.026×10^{-11}
0.001	33.0	73.50	684.70	7.337	4.603×10^{-8}
0.01	32.5	73.50	387.70	2.445	3.507×10^{-3}
0.05	31.0	73.50	351.45	1.848	1.419×10^{-2}
0.1	31.0	73.50	338.85	1.639	2.291×10^{-2}

The following table gives pH values for some dilutions of phosphoric acid solution alone. Plate V shows their graphic representation, with the pH values plotted as ordinates against the cubic roots of the concentrations as abscissae.

Gm. Moles H_3PO_4 per Liter	Temp. °C	Press. Cm.	E.M.F. Millivolts.	pH	cH
0.001	31.5	73.34	423.85	3.051	8.892×10^{-4}
0.01	31.6	73.34	378.70	2.303	4.978×10^{-3}
0.05	26.0	73.55	353.45	1.849	1.416×10^{-2}
0.1	30.0	73.34	336.90	1.598	2.524×10^{-2}

Phosphoric acid was titrated against sodium hydroxide, following the progress of the titration by determining the hydrogen ion concentration after each addition of alkali. Plate VI shows pH values plotted as ordinates against gram moles of sodium hydroxide per gram mole of phosphoric acid as abscissae. The amount of alkali added was recalculated in these terms so that it could be plotted for comparison on a uniform basis with the data of Ringer[1] and that of Prideaux[3]. On Plate VI, the yellow curve represents the work of Ringer, the red that of Prideaux, and the black, the data obtained in this work.

All three curves show decided breaks at the points corresponding to the formation of NaH_2PO_4 and Na_2HPO_4. The

curves of Ringer and Prideaux are smooth through the region where Na_3PO_4 should be formed. This they ascribe to practically complete hydrolysis of the Na_3PO_4, and is also indicated by the decidedly alkaline reaction of solutions of Na_3PO_4 alone. The data obtained in the titration done in the present work, however, gives a slight rise at this point indicating that hydrolysis is not complete here.

Ringer, in his titration, added the designated amount of sodium hydroxide to ten cubic centimeters of his phosphoric acid solution, made the mixture up to one hundred cubic centimeters with water, and determined the pH in a thermostat at 18° C. His original phosphoric acid was 0.14615 molar, so the solutions on which he made his measurements were 0.014615 molar with respect to the phosphate radical. His data follows:

c.c. NaOH	cH	pH	Gm. Moles NaOH per Gm. Mole H_3PO_4
0.00	1.08×10^{-2}	1.967	0.00
6.00	7.55×10^{-3}	2.122	0.2326
12.23	4.50×10^{-3}	2.347	0.4740
18.00	2.32×10^{-3}	2.635	0.6976
22.32	9.83×10^{-4}	3.008	0.8650
24.46	4.12×10^{-4}	3.385	0.9480
25.76	8.15×10^{-5}	4.098	0.9758

c.c. NaOH	cH	pH	Gm. Moles NaOH per Gm. Mole H_3PO_4.
25.76	6.82×10^{-5}	4.166	0.9758
27.47	1.68×10^{-6}	5.775	1.0648
30.	5.78×10^{-7}	6.238	1.1628
34.34	2.32×10^{-7}	6.635	1.3310
38.63	1.15×10^{-7}	6.940	1.4972
39.00	1.13×10^{-7}	6.947	1.5116
42.93	7.30×10^{-8}	7.137	1.6640
44.64	4.78×10^{-8}	7.321	1.7302
48.92	1.78×10^{-8}	7.750	1.8962
51.52	5.97×10^{-9}	8.224	1.9970
51.52	4.68×10^{-9}	8.330	1.9970
53.23	1.71×10^{-9}	8.767	2.064
54.08	1.04×10^{-10}	9.983	2.096
54.08	8.27×10^{-11}	10.083	2.096
54.94	1.95×10^{-11}	10.710	2.130
54.94	4.75×10^{-11}	10.323	2.130
54.94	2.04×10^{-11}	10.690	2.130
56.66	1.08×10^{-11}	10.967	2.196
60.09	5.68×10^{-12}	11.246	2.330
68.68	1.68×10^{-12}	11.775	2.662
77.29	8.71×10^{-13}	12.060	2.996
85.85	5.18×10^{-13}	12.286	3.328

Prideaux carried on his titration only between the points corresponding to the formation of NaH_2PO_4 and Na_3PO_4. The column labeled "Ratio", in his data represents the number of milligram moles of sodium hydroxide to ten milligram moles of phosphoric acid, and is therefore the number of cubic centimeters of normal sodium hydroxide solution to be added to ten cubic centimeters of the normal acid and made up to one hundred cubic centimeters. All of Prideaux's solutions are, therefore, 0.0333 molar with respect to the phosphate radical. To plot his data on the same basis as the other two sets of figures, his ratio numbers must be divided by ten.

Ratio	cH	pH
11.05	1.7×10^{-6}	5.770
14.45	2.6×10^{-7}	6.586
15.50	2.0×10^{-7}	6.699
16.55	1.3×10^{-7}	6.887
17.60	7.6×10^{-8}	7.120
19.97	3.5×10^{-9}	8.456
20.00	1.5×10^{-9}	8.824
20.5	5.9×10^{-11}	10.230
21.0	2.5×10^{-11}	10.603
21.6	2.0×10^{-11}	10.699
21.9	1.3×10^{-11}	10.887
22.2	1.2×10^{-11}	10.921
25.0	2.9×10^{-12}	11.538
30.0	6.8×10^{-13}	12.168

In the titration made in this work, the volume of sodium hydroxide noted was added to 13.63 c.c. of the 0.367 molar H_3PO_4 and the volume made up to 50 c.c. with carbon dioxide free water. All of the solutions were therefore one-tenth molar with respect to the phosphate radical. The data follows:

c.c. NaOH	Temp. °C	Press. Cm.	E.M.F. Milli-volts.	cH	pH	Gram Equivalent NaOH Per Gram Mole of H_3PO_4
	(0.367 molar H_3PO_4 alone)			2.523×10^{-2}	1.598	0.000
2.05	24.2	73.78	348.90	1.746×10^{-2}	1.758	0.198
4.05	24.2	73.78	361.80	1.016×10^{-2}	1.993	0.3915
6.00	24.2	73.78	376.90	5.861×10^{-3}	2.232	0.5802
8.00	24.2	73.78	400.10	2.459×10^{-3}	2.611	0.7734
9.40	24.0	73.58	427.50	8.110×10^{-4}	3.091	0.9090
10.30	24.0	73.58	535.00	1.213×10^{-5}	4.916	0.9960
11.00	25.2	73.58	583.50	1.866×10^{-6}	5.729	1.0635
16.00	25.6	73.58	651.50	1.328×10^{-7}	6.877	1.5471
18.50	25.8	73.58	676.10	4.966×10^{-8}	7.304	1.7889
19.30	26.0	73.58	694.40	2.518×10^{-8}	7.599	1.8660
20.05	26.8	73.58	724.40	7.674×10^{-9}	8.115	1.9386
21.00	27.0	73.58	837.35	1.042×10^{-10}	9.982	2.0304
26.00	27.0	73.58	905.40	7.482×10^{-12}	11.126	2.5440
29.00	26.8	73.58	942.65	1.592×10^{-12}	11.798	2.8041
31.00	26.0	73.58	969.00	5.902×10^{-13}	12.229	2.9973
36.00	25.5	73.58	981.65	3.516×10^{-13}	12.454	3.4806

CALCULATION OF DEGREE OF HYDROLYSIS.

An attempt was made to utilize the data on pages 13, 14 and 15 of this volume for the calculation of the degrees of hydrolysis of the sodium salts of phosphoric acid. This calculation was made from the equation,

$$h = \frac{Coh}{C_s} = \frac{Kw}{cHC_s},$$

where h is the degree of hydrolysis, C_s is the total concentration of salt in gram moles per liter, and cH, Coh and Kw have their usual significances. The results obtained for Na_2HPO_4 were compared with those of Abbott and Bray[10], who used the formula

$$\frac{C_s h^2}{1 - h} = \frac{Kw}{K_A}$$

Their calculations indicate that the degree of hydrolysis of Na_2HPO_4 increases directly as the dilution. The same was found true in the present work for NaH_2PO_4, whose solutions have a higher hydrogen ion concentration than does water. For Na_2HPO_4 and Na_3PO_4, whose solutions have a lower hydrogen ion concentration than does water, the degrees of hydrolysis calculated from the experimental data go through a maximum. Although this is not in accord with the generally accepted views on hydrolysis, it seems logical that this function should follow the same plan as the hydrogen ion concentration of an acid, which increases with dilution to a certain point beyond which increased dissociation fails to compensate for the lesser amount of acid per unit volume. Further, the hydrolysis of a

salt is due to the weakness of the acid corresponding to the anion or the base corresponding to the cation. With increasing dilution, there occurs an increase in the dissociation of the weak acid or weak base formed by the hydrolysis. With increased dissociation, the weak constituent behaves like a stronger acid or base, and hydrolysis, therefore, decreases. Attention may be directed to the fact that the other methods for calculating degrees of hydrolysis do not use directly measured values for hydrogen and hydroxyl ion concentrations. Consequently, it would seem that the experimental method used here should be more reliable than the others.

Conc. in Gram Moles Per Liter	pH	% Hydrolysis
	NaH_2PO_4	
0.12967	6.038	0.00001423
0.064835	6.157	0.00003892
0.025934	6.288	0.00001316
0.012967	6.359	0.0003026
0.004322	6.454	0.001182
0.0025934	6.547	0.002508
0.001854	6.643	0.005029
0.0012967	6.717	0.008204
	Na_2HPO_4	
0.10144	8.902	0.01629
0.05072	8.781	0.02518
0.020288	8.656	0.04211
0.010144	8.549	0.06574
0.003381	8.179	0.07852
0.0020288	8.049	0.1042
0.001449	7.838	0.08842
0.0010144	7.640	0.08107
	Na_3PO_4	
0.090478	12.083	18.48
0.045239	11.891	26.82
0.018096	11.734	47.82
0.0090478	11.513	59.39
0.0050159	11.022	56.95
0.0018096	10.573	38.94
0.0012925	10.327	32.25
0.00090478	10.226	30.01

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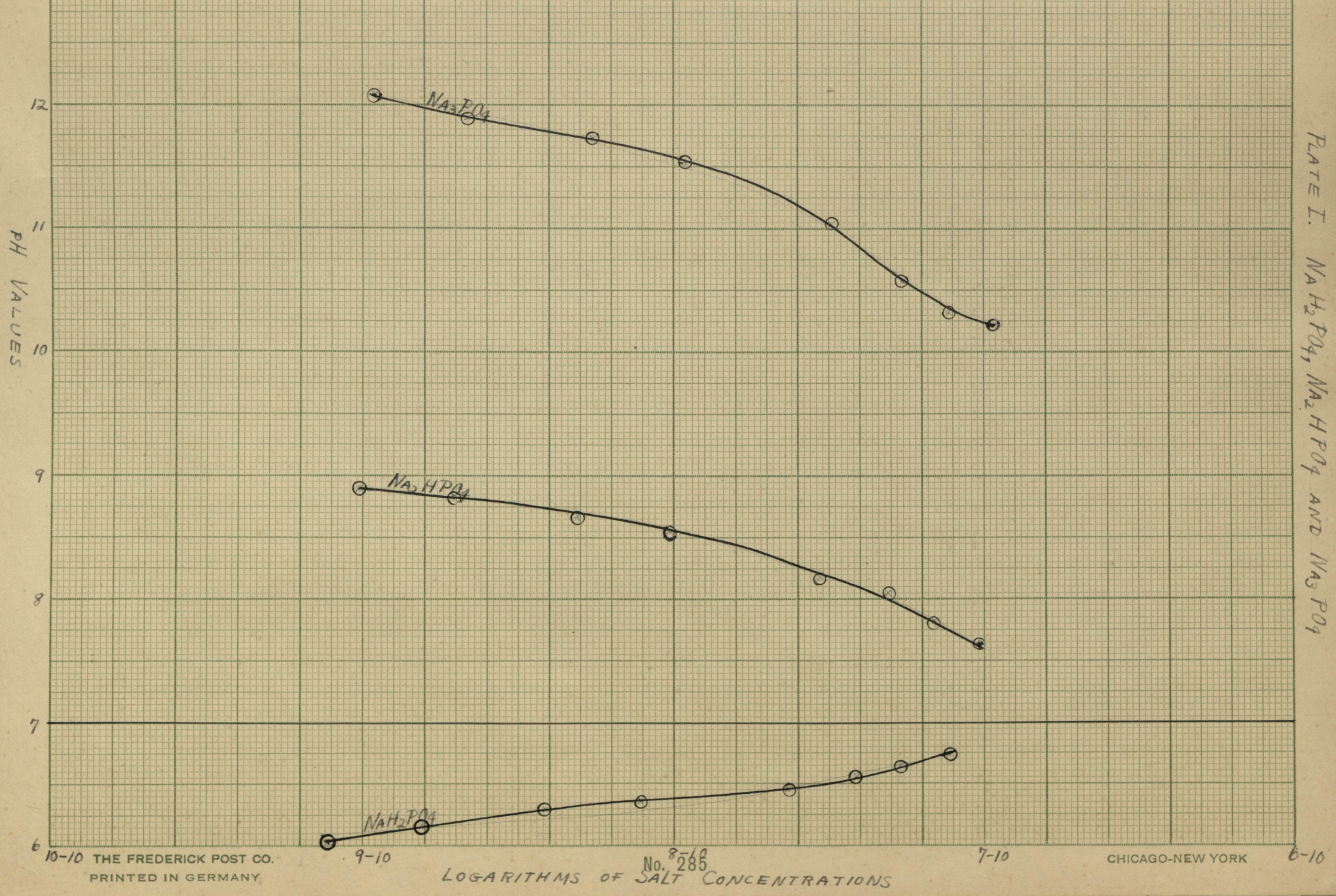

PLATE I. NaH_2PO_4, Na_2HPO_4 AND Na_3PO_4

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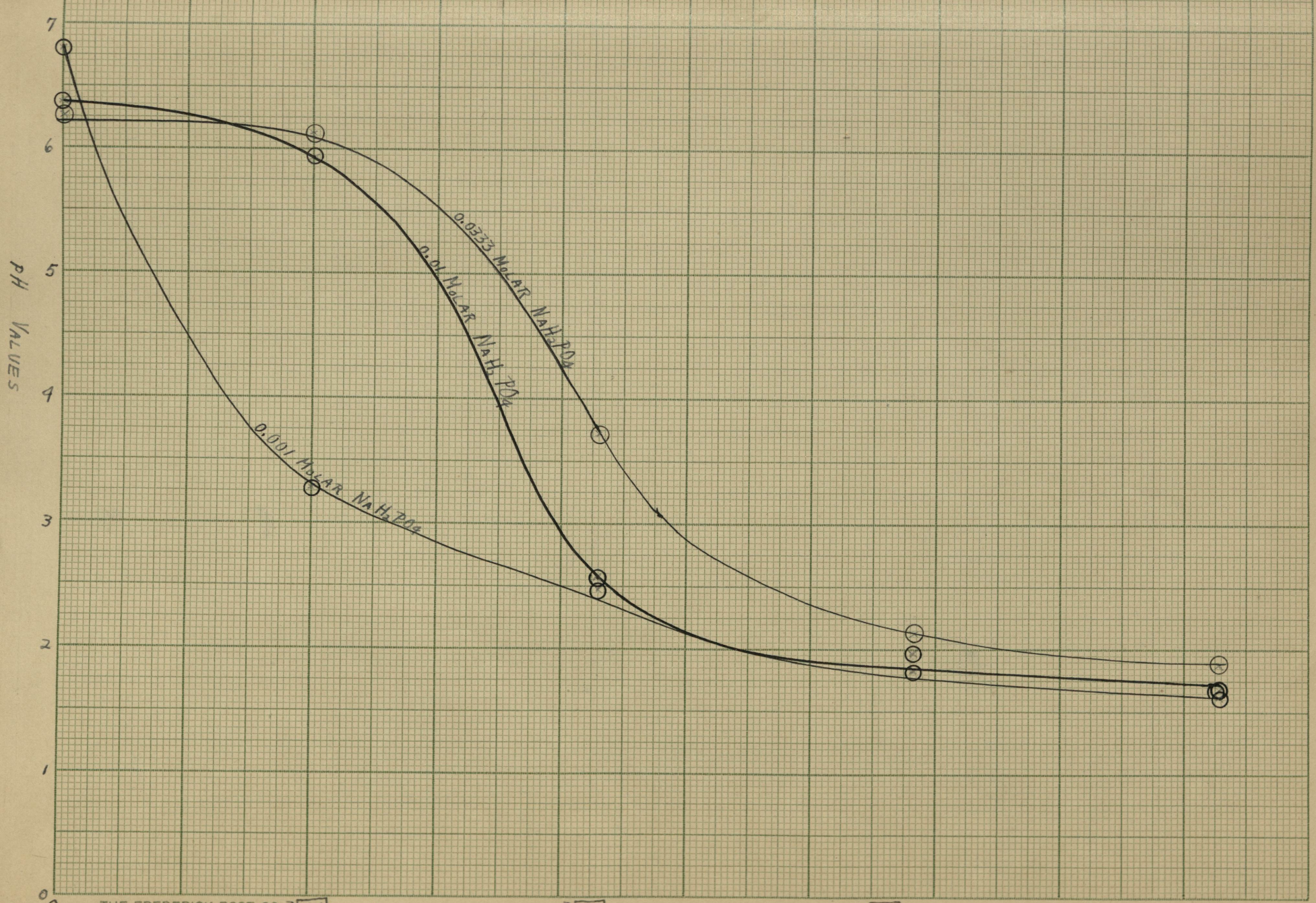

PLATE II $NaH_2PO_4 + H_3PO_4$

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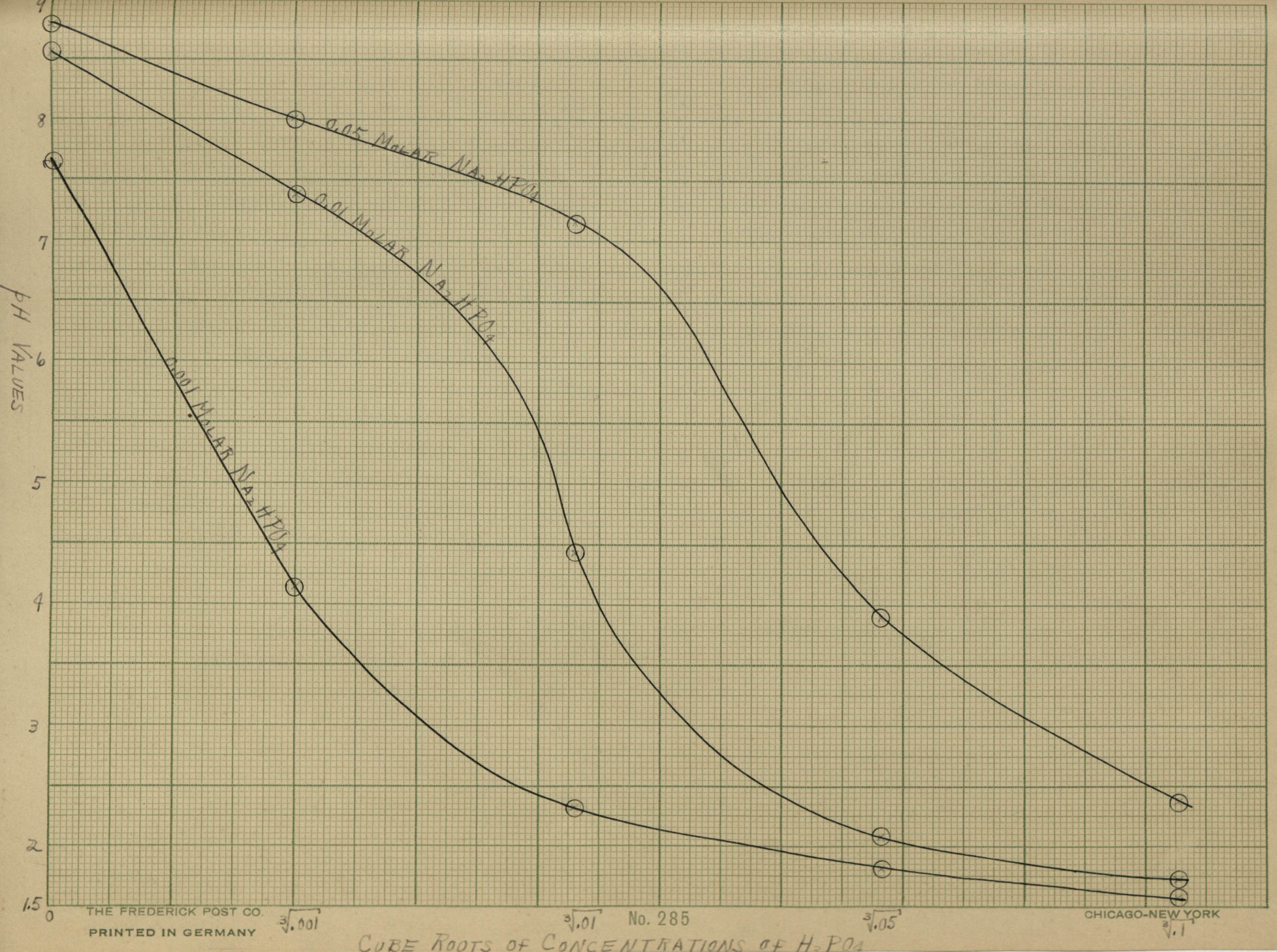
PLATE III Na2HPO4 + H3PO4
PH VALUES
0.05 MOLAR Na2HPO4
0.01 MOLAR Na2HPO4
0.001 MOLAR Na2HPO4
8
7
6
5
4
3
2
1.5
0
∛.001
∛.01
∛.05
∛.1
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CUBE ROOTS OF CONCENTRATIONS OF H3PO4

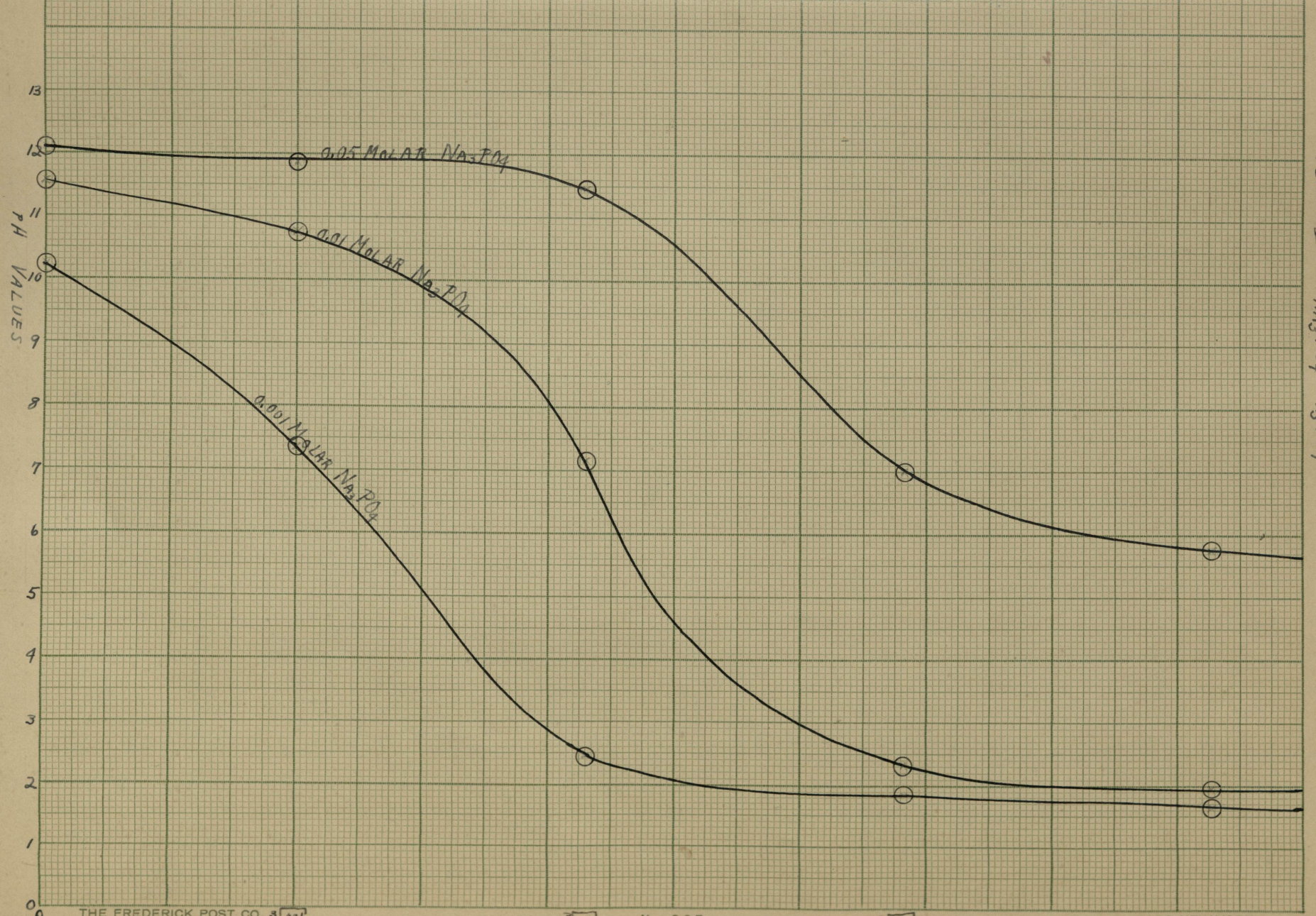

PLATE IV $Na_3PO_4 + H_3PO_4$

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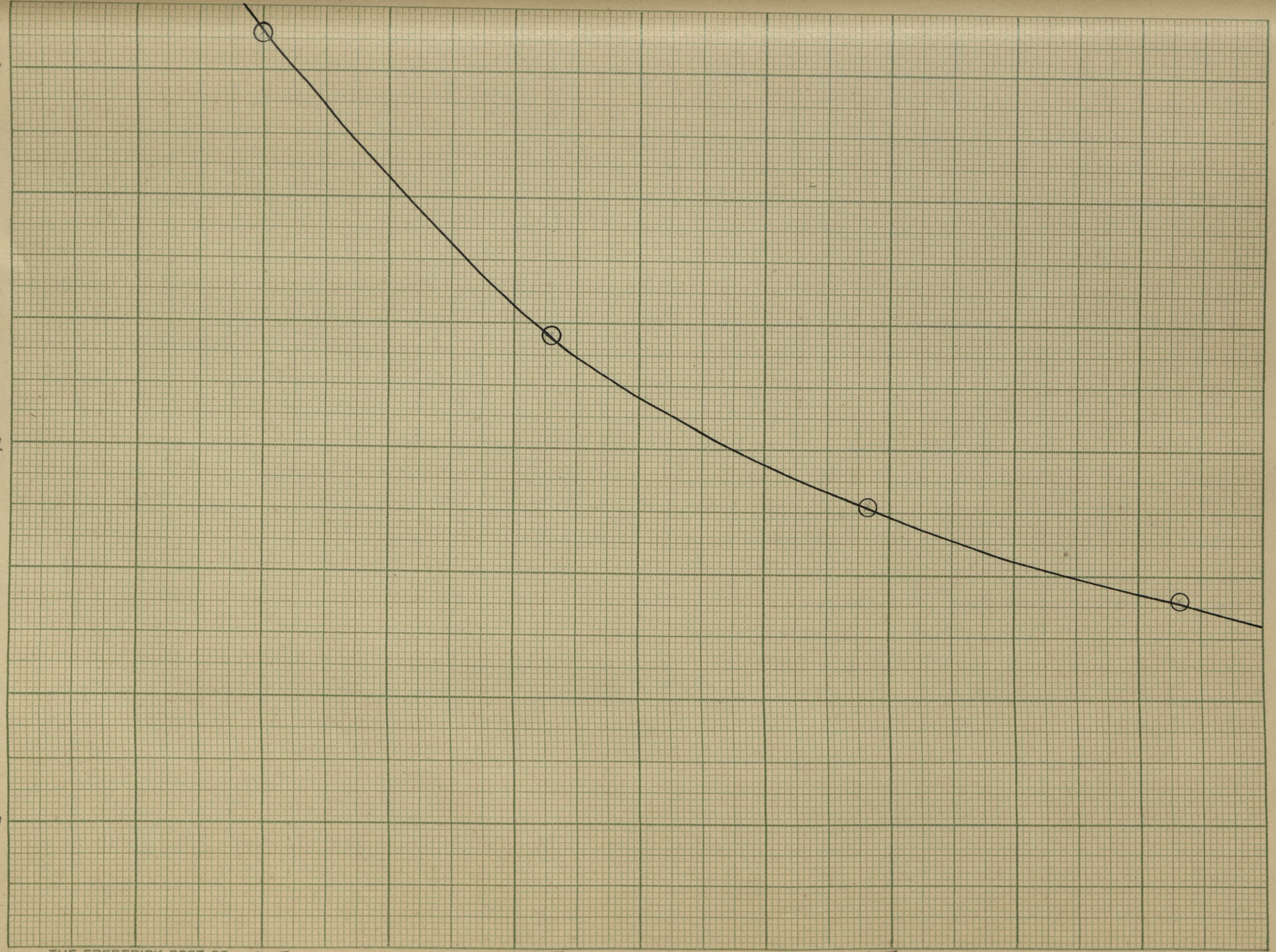
3
2
1
PH VALUES
PLATE II H3PO4
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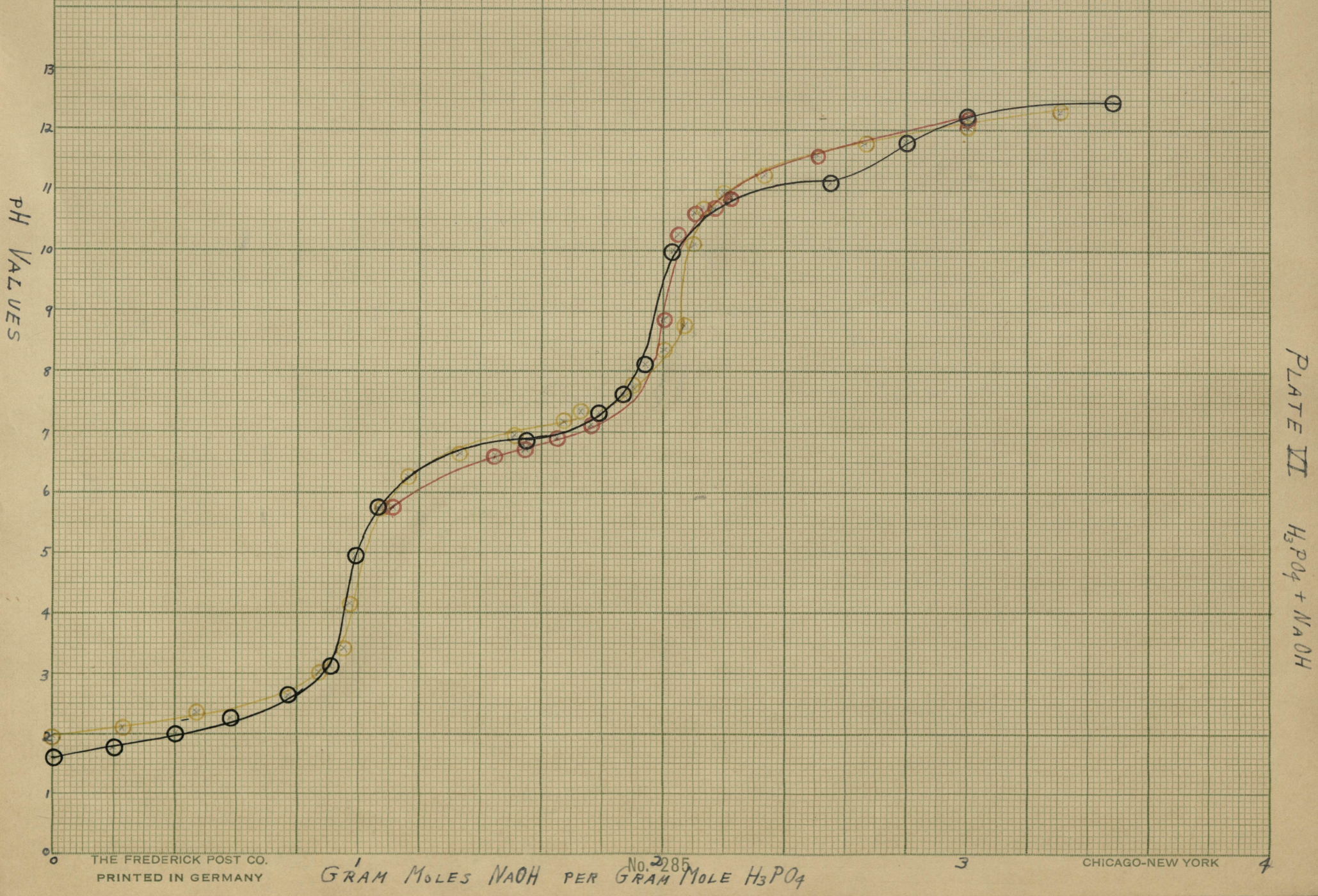
CUBE ROOTS of CONCENTRATIONS


PH VALUES
0
1
2
3
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5
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7
8
9
10
11
12
13
GRAM MOLES NAOH PER GRAM MOLE H3PO4
PLATE VI
H3PO4 + NAOH
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